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Research of Iron-Rich Pellet Oxide Reduction by Carbon

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Abstract. Advantages of iron-rich pellet use in steelmaking in electric furnaces as compared to steelmaking scrap were reviewed. Decomposition of carbon and hydrocarbon oxides with carbon release was observed at the Kachkanar iron-rich pellet cooling in shaft furnaces, where they were reduced. The released carbon interacts with iron oxides and alloying elements. Derivatorgraphic research was carried out, which allowed establishing the temperature ranges of the iron oxide and alloying element reduction process as well as reaction mechanism depending on the carbon amount. To investigate the nature of alloying element distribution among the metal and slag phases a mineralogical analysis was carried out for carbon containing iron-rich Kachkanar pellets.
The carried out research on alloying element (vanadium, titanium, manganese) distribution in Kachkanar iron-rich pellets after their post-reduction allowed process flow development for preparation of charge materials for steelmaking using spongy iron. A process was developed for vanadium and titanium containing alloying element production from iron-rich pellets containing carbon.

1. Iron-Rich Pellet Properties

A currently steelmaking in electrical furnaces is increasingly using iron-rich pellets produced by direct reduction methods [1–11]. The pellet basis is iron with carbon content of 0.2 to 2.0–2.4 %. They also contain some amount of unreduced iron oxides (3–12 %) and lean material which amount shall be no more than 3–7 % of the pellet weight. An important pellet property is metallization degree usually comprising 88–97 %. A distinctive feature of this raw material is low content of sulphur, phosphor, copper, nickel, chrome and other additions usually contained in steelmaking scrap in fairly large amounts. This simplifies the melting process and ensures production of high purity steel. Pellet content in the charge materials comprises 60–70 % of its weight. The reduction process in the course of iron-rich pellet production is carried out in a shaft furnace [12–14], where hydrogen and carbon monoxide coming from natural gas as a result of conversion are used as reducing gas.

When iron-rich pellets are cooled in shaft furnaces carbon and hydrocarbon oxides are decomposed with carbon release. Hence, the reduction products contain soot and carbide carbons and carbon diluted in iron. In Kachkanar iron-rich pellets oxides of iron and vanadium, titanium and manganese alloying elements interact with carbon in steelmaking units when making steel; at that iron and alloying elements are distributed among the metal and oxide phases determining reducing element consumption and carbon formation in the pool. Iron oxide reduction by carbon is accompanied by a significant endothermic effect and substantial energy costs at steelmaking in arc electric furnaces [15–17].

The aim of this work is to study the impact of the initial carbon content in iron-rich pellets on the oxide phase reduction process in Kachkanar pellets with the metallization degree of 88 %. The average chemistry of the pellets under research is shown in Table 1. The carried out derivatographic research

showed that the bulk of iron-rich pellet oxides is reduced at 1000–1300 ˚C by carbon, diluted in iron; at that the reaction mechanism significantly depends on the carbon amount. Thus, iron-rich pellet use in steelmaking units requires knowledge of the quantitative dependence between the carbon consumption degree, time and temperature in the stated temperature range.

2. Iron Rich Pellet Reduction

The reduction process of residual oxides in iron-rich pellets by carbon may be conceptually described by a generalized kinetic equation [18]. However, the obtained formulas will be of empirical nature rather than theoretical [19]. They will provide no answer to the question of which oxides are recovered by carbon. At the same time the distribution pattern of alloying elements among the metal and slag phases determines the mechanism of the secondary reduced iron-rich pellet use in steelmaking units.

The obtained results are indicative of the fact, that iron, titanium and vanadium oxides which may interact with carbon are not in pure form, but are binded into complex compounds and glass. The latter amount depends on the melt content at the pellet firing at the Kachkanar Mining and Processing Works, as the metallization temperature in shaft furnaces is below the liquid phase temperature. Study of the mineralogical composition changing in the course of Kachkanar iron-rich pellet reduction by carbon showed that non-metallic phase in such pellets is extremely fine what complicates the mineralogical analysis of samples subjected to thermal reduction treatment. It was also detected that alloying and slag-forming elements were redistributed particularly in the samples with the initial content of 2.63 and 5.20 % C, the slag phase contained Ca, Mg, Al, Ti, V, Si. Besides, calcium titanate and magnesium vanadate inclusions were noted. Titanium-vanadium spinel cemented with dolomite glass was noted in the samples with 2.68 and 2.09 % C at 1320–1350 ˚C.

It may be concluded that some titanium and aluminium from spinel compounds in initial iron-rich pellets transfer to iron-free compositions. It is possible only in case of iron oxide reduction from metal spinels, besides the noted inclusions of unbound silica in the reduced samples, absent in the initial samples, are indicative of metallic iron formation from iron-calcium-silicate glass. Review of vanadium distribution in the reduced pellets demonstrated that the attempts to distinguish particular mineralogical forms with its presence (except for insignificant amounts of titanium-vanadium spinel) failed. Its uniform inclusions in the metallic iron matrix are noted.

The carried out mineralogical analysis showed that carbon at heating of iron-rich pellets from Kachkanar concentrate is predominantly consumed for Fe and V reduction to the metallic state from glass and spinels, at that the remaining Ti and Al oxides are bound with Ca and Si. The mineralogical analysis is of qualitative character and provides no data on alloying element content in the metallic and oxide phases. At the same time this data is required to develop the process of metallurgical Kachkanar pellet use in steelmaking.

Table 1. Average Chemistry of Kachkanar Pellets.

Pellet Type	Content, %							
	SiO_2	C	Al_2O_3	CaO	MgO	FeO	$Fe_{tot.}$	Fe_2O_3
Initial, fired	3.54	0.10	2.39	2.78	2.59	2.86	61.41	84.64
Iron-rich	3.34	2.53	2.53	2.16	2.75	11.89	80.84	–
	Content, % (continued)							
	Fe_{met}	V_2O_5	P_2O_5	TiO_2	Cr_2O_3	MnO	S	$\frac{CaO}{SiO_2}$
Initial, fired	0.18	0.57	0.04	2.94	0.10	0.23	0.003	0.79
Reduced	71.60	0.72	0.05	3.30	0.11	0.29	0.004	0.65

Please find below the research results on alloying element distribution in Kachkanar metallurgical pellets after their post reduction by carbon. From the previous mineralogical analysis one shall expect the predominant titanium accumulation in the slag phase of iron-rich pellets after their post reduction and partial vanadium transfer to iron. To evaluate Ti, V and Mn reduction degree their content in the slag metallic fractions obtained by sieving of crushed iron-rich pellets after their reduction was determined by chemical analysis. The pellets reduced in a pilot furnace of the Beloretsk Metallurgical Works containing in %: 3.7 of C and 12.4 of FeO; 1.8 of C and 12.1 of FeO were used for the experiments. The metallized iron products were heat treated at 1100 – 1350oC in an open coal heater furnace (weakly oxidizing atmosphere with 1 % of O2 in the mixture with CO, CO2 and N2) and in a controlled-atmosphere furnace, filled with argon and pumped down to 10-8 Pa. Pellet batch (50 – 100 g) in an alumina crucible was placed into a preliminary heated furnace and held at the preset temperature for 1 h. After cooling the pellets were weighted, crushed and sieved into fractions, mm: coarse of over 2.5, medium of 1.0 – 2.5 and fine of less than 1.0.

As per derivatographic analysis in the course of heat treatment the sample weight reduced as follows, %: in weakly oxidizing medium – by 1.8–3.5, in argon atmosphere – by 2.0–3.7, in vacuum – by 3.4–6.6. Together with reduction the metallic iron sintered and coagulated; melt drips showed up on crack and pore surface. The reduced pellet observation results showed that in atmosphere containing CO the pellets were welded already at 1250 ˚C, moreover the process was accompanied by liquid metal medium release. Argon and vacuum welding temperature is 50 ˚C higher. The stated phenomena are related to various degrees of carbon consumption for Fe, V, Mn, Ti oxide reduction within the research temperature range by carbon, diluted in iron, and carbides in reactions:

$$[C]_{met} + (Me_nO_m) \rightarrow [Me]_{Fe} + \{CO\}; \quad (1)$$

$$[C]_{Fe} + (Me_nO_m) \rightarrow [Me_xC] + \{CO\}; \quad (2)$$

$$[Fe_3C] + (Me_nO_m) \rightarrow [Me]_{Fe} + [Me_kC_1] + \{CO\}. \quad (3)$$

As the product of these reactions is CO, its presence in gas phase shifts the balance to the left and ensures larger amount of carbon residue. The latter reduces the iron melting temperature and the obtained melt causes pellet adhesion. Absence of gaseous reaction products (1)–(3) in argon and particularly in vacuum results in rapid carbon consumption and iron melting temperature increase. This allows pellet maintaining without adhesion within the range of 1250–1300 ˚C, where manganese and vanadium carbide solubility in austenite is comparatively high [20], and these elements may to a significant extent transfer to the metallurgical phase. Titanium carbide solubility in iron-rhodic alloys is negligible, thus ferrous titanium spinel reduction causes Ti binding with other pellet components, such as lime, with calcium titanate formation. This is confirmed by data on V, Ti, Mn alloying element dependence on iron content in slag metallic fractions of various size. It was determined that in case of comparatively high C concentration in the pellets (~3.7 %) at 1200–1300 ˚C the V content is the same in high ferriferous and low ferriferous fractions. At the same time with low C content (~1.5 %) the low ferriferous fraction is enriched with vanadium. These results correlate with mineralogical research data where it was stated that in initial iron-rich pellets vanadium is predominantly bound with slag, and at high temperature reduction by carbon it partially transfers to iron.

The similar picture is observed with regard to manganese but only for atmospheres containing no CO, where reduction is the most intensive. Titanium behaves differently: low ferriferous fractions pellets with high C content (~3,7 %) contain 5–6 times more Ti, what expressly speaks of its concentration in slag inclusions.

Thus, in the course of nonoxidation heating of carbon containing iron-rich pellets vanadium reduction is the most intensive, at that high degree of its transfer into metal is observed for all studied gaseous media. Mn is reduced to a lesser extent and Ti reduction is absolutely insignificant. However, all elements are reduced in vacuum.

Assuming that alloying elements are completely absent in initial iron-rich pellets, V, Mn, Ti reduction degree was calculated. The amount of the reduced elements was determined based on their content in the most ferriferous (90 % Fetot) fraction with the size of over 2,5 mm. As its yield is quite high and comprises 70–80 %, thus error due to alloying element losses in slag metallic fractions with low iron content is insignificant.

Research on post reduction of iron-rich Kachkanar pellets allows recommending of the process flows using spongy iron. It is difficult to reach high metallization degree of Kachkanar pellets in shaft furnaces because of the occurred dense layer of metallurgical iron, preventing diffusion of gaseous reducing agents. Production of pellets containing over 70–75 % of Femet, is related to significant losses of shaft furnace performance. At the same time soot carbon evolved at cooling is highly soluble in iron, allowing active post reduction of practically all oxide inclusions.

Use of carbon reduction potential allows reduction of power consumption in electric steelmaking furnaces due to smaller amount of heat consumed for reduction and slag yield. Preliminary post reduction also allows homogenising of the pellet composition with regard to carbon and stabilizing the melt process conditions.

Based on the obtained results it is clear that iron-rich pellets shall be preliminary heated in atmosphere precluding oxidation of spongy iron with the minimum amount of CO, what will allow intensification of iron and alloying element reduction.

Technically the most real is the atmosphere, containing 0.1–1.0 % of O2 and less than 1 % of CO. It may be obtained in drum furnaces when burning gas with excess air factor of about 1.02–1.05. The stated atmosphere composition will allow pellet heating temperature increase to 1250–1300 ˚C without their fusion and ensure free movement of the material from the furnace.

Heating to the stated temperatures with the rate of 10–15 ˚C/min will allow complete post reduction. At that the pellets will get into the temperature zone of possible melt formation (over 1250 ˚C), the carbon consumption degree will comprise 0.8–0.9. This will preclude iron carbonization and liquid phase release. The higher heating rates of the pellets are hardly allowable as they increase the carbon residue content at the temperature of over 1250 ˚C and cause material fusion. Heating rates of over 10 ˚C/min. will result in reduced drum furnace performance and increased conversion costs. Preliminary reduction of charge materials containing spongy iron is more efficient in drum furnaces than in steelmaking furnaces.

It shall be noted that the considered method is acceptable for pellets, containing alloying elements V, Mn, which oxides are easily reducible and carbides are freely soluble in iron, Ti remains in slag and drains with it. Processing of these slags with low Ti is hardly profitable. At the same time the obtained results show the actual way of richer titanium master alloy production particularly for pellets with high TiO_2 content.

The research results show that after heat treatment of iron-rich pellets containing C and V and Ti oxides in weakly oxidizing medium at 1250–1300 ˚C, vanadium was predominantly in the metallic phase and titanium – in the slag phase, thus after crushing of such pellets the metallic magnetic phase was enriched with vanadium, and less magnetic phase with large slag amount – with titanium. Separation of these phases and the corresponding master alloy production by magnetic separation is quite acceptable. Fineness, type and operating conditions of magnetic separators shall be selected to develop the corresponding process.

3. Summary

The reduction process of Kachkanar iron-rich pellets by carbon released at their cooling in gasses containing carbon oxides and hydrocarbons was studied. Reduction temperatures of the bulk oxides in iron-rich pellets were determined by the derivatorgraphic method. Mineralogical analysis of carbon bearing iron-rich pellets was carried out with a view of studying the nature of alloying element distribution between the metallic and slag phases. To use the reduction potential of soot carbon post reduction of oxide inclusions in iron-rich pellets was suggested in rotating furnaces prior to their getting

into electric steelmaking units. A process was developed for vanadium and titanium containing master alloy production from carbon containing iron-rich pellets.

References

[1] Shnabel S 2004 From Direct Reduction Iron to High Quality Steel *Ferrous Metals* **6** 20–23
[2] Kudryavtsev V S and Pchelkin S A 1974 *Iron-Rich Pellets* (Moscow: Metallurgy)
[3] Yusfin Yu S, Danshin V V, Pashkov N F and Pitatel V A 1982 *Iron Ore Raw Material Metallization Theory* (Moscow: Metallurgy)
[4] Shvydky V S, Yaroshenko Yu G, Spirin N A and Lavrov V V 2018 Simulation of Iron-Rich Pellet Firing Process with Due Account for Their Physicochemical Transformations *Bulletin of Sibir State Industrial University* **4(26)** 36–40
[5] Kozhukhov A A 2012 Research of Iron-Rich Pellet Role in Slag Frothing in State-of-the-Art Arc Steelmaking Furnaces *Electrometallurgy* **11** 11–16
[6] Kozhukhov A A, Merker E E, Sazonov A V 2010 Review of Arc Furnace Heat Exchange at Iron-Rich Pellet Melting *University Bulletin. Ferrous Metallurgy* **5** 37–40
[7] Grishin A A 2006 Particular Features of Metal Decarbonisation at Continuous Feeding of Iron-Rich Pellets to Arc Furnace Pool *University Bulletin. Ferrous Metallurgy* **11** 21–23
[8] Sazonov A V, Merker E E, Kochetov A I 2008 Particular Features of Metal Decarbonisation at Pellet Melting in Arc Furnace *University Bulletin. Ferrous Metallurgy* **12** 27–29
[9] Kraht A N, Merker E E, Kem A U and Stepanov V A 2015 Reduced Iron Ore Pellets and Efficiency Increase for Their Use in Electric Steelmaking in Arc Furnace *Don State Technical University Bulletin* **3(82)** 35–40
[10] Merker E E and Stepanov V A 2014 Electric Steelmaking Efficiency Increase by Metallized Raw Material Feeding to High Temperature Zone through Channels in Arc Furnace Electrodes *Ferrous Metallurgy* **1** 41–49
[11] Amdur A M 1979 *Research on Thermotechnical Features of Iron-Rich Pellet Melting in Arc Steelmaking Furnaces* (Sverdlovsk: Ural Polytechnic University named after S. M. Kirov)
[12] Povolotsky V U, Lantsov U V, Plotnikova S U 2014 Kinetic and Dynamic Model of Direct Iron Production in Shaft Furnace *Steel* **8** 35–38
[13] Zinyagin G A, Sushkov P N 2004 Research and Process Development of Direct Iron Production in Shaft Furnaces at Charge Material Increased Sulphur Content *University Bulletin. Ferrous Metallurgy* **1** 13–16
[14] Grebennikov V S 1982 *Optimization of Iron-Rich Pellet Production Process in Shaft Furnaces* (Moscow: National University of Science and Technology MISIS)
[15] Merker E E, Sazonov A V and Grishin A A 2008 Particular Features of Iron-Rich Pellet Electric Melting in Arc Furnace *University Bulletin. Ferrous Metallurgy* **2** 31–33
[16] Fedina V V, Merker E E, Kharlamov D A 2004 Improvement of Metallized Iron Ore Raw Material Electric Melting Process in Arc Steelmaking Furnace *Ferrous Metals* **2** 16–19
[17] Nokhrina O I, Rozhikhina I D, Rybenko I A and Khodosov I E 2016 Fundamental Development of High Efficiency Metallization Processes Using Thermodynamic Simulation *University Bulletin. Ferrous Metallurgy* **4(59)** 237–244
[18] Uendlandt U 1978 *Thermal Analysis Methods* (Moscow: Mir)
[19] Delman B 1972 *Heterogenous Reaction Kinetics* (Moscow: Mir)
[20] Golikov I N, Goldshtein M I, Murzin I P 1968 *Vanadium in Steel* (Moscow: Metallurgy)